



TITLE:

Synthesis of Dimethylformamide from Methanol, Ammonia and Carbon Monoxide under High Pressure

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CITATION:

Takezaki, Yoshimasa ...[et al]. Synthesis of Dimethylformamide from Methanol, Ammonia and Carbon Monoxide under High Pressure. Bulletin of the Institute for Chemical Research, Kyoto University 1961, 39(4-5): 326-327

ISSUE DATE:

1961-11-15

URL:

<http://hdl.handle.net/2433/75846>

RIGHT:

ABSTRACTS

2) Effect of CO pressure (560~1030 atm., MeOH 0.5M, BF₃·4H₂O 0.125M, 335°C):

The initial rate is proportional to the fugacity of CO, and the yield is over the stoichiometrical amount of BF₃, for instance 0.4M of AcOH is produced under 860 atm. of CO and 0.125M of BF₃ in 2hrs.

3) Effect of temperature (320~360°C, CO 800atm., MeOH 0.5M, BF₃·4H₂O 0.125M): Initial velocities $(dx/dt)_{t=0} \times 10^3$, are 26.2 at 360°C, 10.6 at 340°C and 4.4 at 320°C.

4) Effect of MeOH charge amount: Under the fixed conditions of 335°C, 800~850 atm. and BF₃ 0.125 M, the yield drops the charge of MeOH is raised, for instance 97% yield for charged MeOH 0.5M and 1 hr., but only 10% for charged MeOH 1.0 M in a reactor of 130 c.c.

The linear relationship is obtained between the initial velocity and MeOH equilibrium concentration in the liquid.

5) From the above-mentioned results, the initial rate equation has been obtained as shown next:

$$(dx/dt)_{t=0} = (kf_{co}k'_m/4aeV_f) [-(m/M_0) + \{(m/M_0)^2 + (8ae/M)^{1/2}\}]$$

where, x =produced AcOH/charged MeOH(M/M),

$$a = K^2RT/P_{H_2O}V_f, \quad b = RTV_i/V_f, \quad m = 1 + k'_mb,$$

$$e = 1 + k'_eb, \quad a = 9060/V_f, \quad b = 49900/V_f,$$

M =charged MeOH (M), V =free space of autoclave.

Rate constants k 's have been calculated to be 3.97×10^{-5} (atm⁻¹. min⁻¹.) at 350°C, 2.37×10^{-5} at 335°C and 1.62×10^{-5} at 320°C. The activation energy of 22Kcal./mol. has been obtained.

Synthesis of Dimethylformamide from Methanol, Ammonia and Carbon Monoxide under High Pressure

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*Kogyokagaku Zasshi (Journal of the Chemical Society of
Japan, Industrial Chemistry Section), 63, 1739 (1960)*

The effects of reaction conditions on the one step synthesis of dimethylformamide from MeOH, NH₃ and CO have been studied under high pressure in the presence of AcOK as a catalyst. Stoichiometrically the reaction is represented as below, but it is very interesting to know whether the reaction proceeds in one step or in two steps, i. e. methylation followed by formylation.



1) The effect of reaction temperature (220~340°C): The increase of DMA yield and the decrease of MMF and DMF above 280°C are due to the instability

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of DMF. From the fact that the decrease in the yield of FA, MMF and DMF is accompanied with the increase of free amines, it is inferable that MMF and DMF are not produced by the direct methylation of FA.

2) The affect of charge mole ratio NH_3/MeOH : The yield of mono and dimethyl compounds varies in proportion to the mole ratio NH_3/MeOH , but the dimethyl compounds begin to disappear for NH_3/MeOH 1.5. For the low NH_3/MeOH , remarkable amount of trimethylamine (TMA) is produced and MeOH is completely consumed. From this fact, together with the stability of DMF under the compressed CO, we presume that the methylation foregoes the formylation.

3) The effect of CO pressure: It is very interesting that monomethylation does not occur and only dimethylation occurs to some extent in the absence of CO. Moreover, the peculiar phenomenon is found that the methylation proceeds as the rise of CO pressure, whereas it ceases at 400 atm.

4) The effect of catalyst amount and some solvents: AcOK is supposed to be an effective catalyst for the methylation, because a remarkable increase of mono and dimethyl compounds formation is observed even when the trace of this substance is added.

But, above the mole ratio $\text{AcOK}/\text{MeOH}=0.04$, the methylation is complete and no more DMF is formed. In the presence of a large amount of NH_3 and MeOH, without catalyst and solvent, the commencement of the pressure drop delays, and the reaction rate is small, but appreciable amount of FA, MMF and DMF is produced.

When glycerin or water is used as solvent, the yield of MMF and DMF is the same as in the case of AcOK catalyst. So, FA seems to be effective as a solvent.

5) Replacement of FA as the starting material for NH_3 : The yield of DMA from NH_3 is larger than that from FA, and the total amount of mono, di, and trimethyl compounds decreases as the increase of CO pressure. So, it seems quite probable that the reaction proceeds in the order of $\text{NH}_3 \rightarrow \text{amine} \rightarrow \text{amide}$.

6) Conclusion: a) Optimum condition. 280°C , CO initial pressure 500 atm., $\text{NH}_3/\text{MeOH}=1.2$ (mole ratio), $\text{AcOK}/\text{MeOH}=0.03$ (mole ratio), MeOH charge 0.6 M/100 c.c. autoclave; yield (in 3 hrs.), DMF 42%, MMF 34% (MeOH base). b) The reaction is supposed to proceed by $\text{NH}_3 \rightarrow \text{amine} \rightarrow \text{amide}$ in the liquid phase, where FA serves as the solvent.

Acetylation of Cotton Fabric by the Liquid Phase Method

Waichiro TSUJI, Ryoza KITAMARU and Yasuyoshi SAKAGUCHI

*Sen-i Gakkaishi (Journal of the Society of Cellulose and
Textile Industry, Japan)*, **16**, 1021 (1960)

Cotton fabrics were acetylated up to a wide degree of substitution by the liquid phase method as reported in the above journal (1957) by Sakurada and Sakaguchi.